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# Shipboard techniques based on flow injection analysis for measuring dissolved Fe, Mn and Al in seawater†

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An overview is presented of sampling techniques and flow injection analysis (FIA) methods for low concentrations of Fe, Mn and Al in filtered seawater. On the basis of sampling procedures, filtration techniques, accuracy, blanks, detection limits, intercalibration results and oceanographic consistency, the feasibility of these FIA methods was evaluated. It was found that these metals could be measured on board with a minimum risk of contamination and with good accuracy even at low subnanomolar levels ( $<0.5$  nM). Results for reference seawater were in the case of Fe-FIA and Mn-FIA in excellent agreement with the certified values. Data from samples analyzed by Fe-FIA and by cathodic stripping voltametry (CSV) compared well, as did Mn-FIA and GFAAS. All three methods gave results that were mostly in good agreement with data from the same ocean regions published by other research groups. Two different types of surface water sampling were also tested and compared, namely conventional hand filling of a sample bottle from a rubber dinghy away from the ship, and underway pumping of seawater using a 'tow fish'. The latter method gave the best results. Also, conventional membrane filtration and cartridge filtration for large volume filtration were compared using Fe and Al data from water column samples. Good agreement was found for both filter types, although for defining dissolved metal species the latter filter type was preferred.

## Introduction

### Importance of Fe, Mn, Al

Fe, Mn and Al are the most abundant metals in the earth's crust,<sup>1</sup> but only exist at trace levels in the oceans due to their low solubility in oxygenated seawater.<sup>2</sup> Pathways by which these metals can be delivered to the ocean are deposition of aerosols, fluvial input, hydrothermal venting and diffusion/resuspension from (anoxic) seafloor sediments.<sup>1</sup> Fe and Mn are important trace nutrients for marine phytoplankton as they serve both in the photosynthetic pathways and as co-factors for many enzymes in the cell.<sup>3–5</sup> Al has no known metabolic function, there is however evidence that Al incorporated in the silicon frustules of marine diatoms enhances the sturdiness of the cell wall by slowing the biogenic silica dissolution rate.<sup>6</sup>

During the late 1980s the development of sensitive analytical tools and improved trace metal clean methods, played a major role in advancing marine trace metal studies.<sup>7</sup> This led for instance to the revival of the iron limitation hypothesis<sup>7,8</sup> for oceanic phytoplankton species, which in turn had a major influence on our perception of global climatic change. There is a great interest in determining background levels in the world's oceans and to monitor trace metals during transient events such as phytoplankton blooms, atmospheric dust depositions, the melting of sea-ice and deep-sea hydrothermal vents.

### Existing techniques

A practical distinction between land-based and shipboard techniques for trace metal determinations can be made, mainly

based on the size of the analytical apparatus and/or its ability to withstand shocks and vibrations. To the first category belongs for instance the widely used graphite furnace atomic absorption spectrophotometer (GFAAS), which cannot be used at sea, hence the preceding matrix separation–preconcentration using dithiocarbamate–chloroform (or freon) extraction with nitric acid digestion or back extraction<sup>9–11</sup> is better done in the home laboratory. A method using in-line preconcentration with GFAAS detection has been reported.<sup>12</sup> Quite recently, inductively coupled plasma mass spectrometry (ICP-MS) applications have become available for seawater analysis. These are either direct methods or involve a matrix separation–preconcentration step.<sup>13–15</sup>

Ever since shipboard methods were required for tracing hydrothermal plumes by their elevated Mn concentration<sup>16</sup> there has been a drive towards designing direct shipboard analytical methods. When obtaining (near) real-time data one is able to adjust the research program immediately, also any inadvertent contamination would immediately be visible. For example, in shipboard phytoplankton incubations the metal concentration in the cultures is verified, and when too high the experiment can be attempted once again. Another development is underway, monitoring during research cruises with high spatial resolution. Such considerations have been the driving force behind the development of shipboard methods such as flow injection analysis (FIA) or voltametric methods like cathodic stripping voltametry (CSV).

The study of trace metals in the sea is a relatively young discipline, where due to rapid development of methodologies the standardization and certification of methods is still in its infant stage. In order to be able to gather reliable data, quality assurance is inevitable.

Sampling, sample manipulation, choice and use of labware in

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accordance with now well-defined anti-contamination procedures (see, for example, refs. 9, 11 and 17).

Standardization of filtration pore size for the determination of the dissolved fraction of trace metals in seawater. This is an important matter in view of the comparability of data sets, and has not been settled yet. Commonly, 0.1, 0.2 or 0.4  $\mu\text{m}$  pore sizes were used over the years. A tendency towards the utilization of 0.2  $\mu\text{m}$  filters can recently be discerned, although nowadays some research groups claim that cross-flow ultra-filtration techniques are the only way to separate truly dissolved metal species from particulate fractions.

Standardization of sample preservation: acidification of the sample, usually to  $\text{pH} < 2$  (possibly in combination with UV-digestion), to ensure dissolution of colloidal metal species; to break down organic metal complexes and to maintain the long term solubility of the analyte in the sample bottle.

Use of the purest reagents, either available from commercial sources or purified in the laboratory, e.g. by extraction or distillation.

Complete recovery of the analyte, meaning that the detectable amount of analyte is maximal. This is an important issue when preconcentration is involved. One hundred percent of the analyte, or anything near to that, should be recovered and arrive in the detector.

Constancy of sensitivity of the applied analytical methods over time and in space. For a worldwide application of a method it should behave the same always, no matter what seawater matrix will be encountered.

Quality control by regular intralaboratory and interlaboratory accuracy checks, using external reference materials, when available.

Even when taking all these measures, the final data still is to be viewed with scepticism as inadvertent contamination, wall adsorption and various other interferences cannot be ruled out. Independent support for the accuracy of data may be pursued by verifying *oceanographic consistency*<sup>18</sup> meaning that observed trends should correlate with observations of other oceanographic parameters, e.g. hydrography, physics, biology, or chemistry. For example, the widely acknowledged breakthrough in analyses of trace metals in the sea was the observed close correlation of several metals with well known major nutrients.<sup>19,20</sup> However, more often than not, the right variables for comparison have not been measured for the same samples. Another thing the analyst can do is to look at other data sets from nearby locations, if any. This approach is also inconclusive as spatial, seasonal or annual variability could hamper comparability.

In this paper we report on work done to obtain acceptable data quality for Fe, Mn and Al in filtered seawater, based on FIA. After a general description of sampling methods and instrumentation, the analytical qualities of each FIA application are treated in more detail, together with results comparing two filtration methods.

## Experimental

### Sampling methods

Surface sampling was done by a peristaltic pump delivering seawater through a plastic tube that was attached to a tow fish. Contamination from the ship was avoided by towing the fish at  $\sim 1$  m depth at  $\sim 5$  m distance alongside the ship.<sup>17</sup> Analytical work was done in a positive pressure class 100 clean air van equipped with laminar flow hoods. For in-line filtration a Sartobran PH (Sartorius, Germany) cartridge filter was used, containing a 0.45  $\mu\text{m}$  polypropylene pre-filter and two cellulose acetate 0.2  $\mu\text{m}$  main filters. As cartridge filters are manufactured from trace metal clean materials, as well as rinsed with 1 M HCl and ample amounts of MQ (Millipore Milli-Q deionized water  $> 18 \text{ M}\Omega \text{ cm}$ ) and seawater before sampling

starts, a systematic filter blank is deemed to be not necessary. By using the nominal 0.2  $\mu\text{m}$  size cut-off we operationally separate 'dissolved' metal species (truly dissolved, but also colloidal, (in)organically complexed) from suspended particulate matter.

Acidifying the filtrate to  $\text{pH} 1.8$  releases all but the most refractory metal phases into the dissolved form. This acidifying step still necessitates us to take discrete samples which then are left for at least 1 h before further processing. Currently we are assessing the efficiency of in-line acidification as a function of the added acid, the length of delay-mixing coil used and the intensity of the additional UV irradiation (to nullify metal-organic associations). Obviously more aggressive (photo)-chemistry is needed to compensate for the shorter than 1 h residence time in the reaction coil.

For the sampling of the water column,<sup>11</sup> modified Teflon-coated PVC GoFlo samplers (General Oceanics, Miami, USA) of 11 l were mounted on 5000 m  $\times$  6 mm diameter Kevlar hydrowire which was lowered from its deck-winch. At depth, the samplers were tripped by Teflon messengers with a stainless steel core. Inside the clean air van, seawater was in-line filtered through either polycarbonate membrane filters (47 mm diameter) with a pore size of 0.2  $\mu\text{m}$  in Teflon filter holders, or the Sartorius Sartobran cartridge filters. For both types of filtration moderate nitrogen pressure was applied to the GoFlo's: 0.5 bar for membrane filtration (MF), but only 0.1 bar for cartridge filtration (CF). For latter filter type the back pressure due to clogging is much lower because of the much larger area of this filter type (1000  $\text{cm}^2$  versus 17  $\text{cm}^2$  for a membrane filter). The use of cartridge filters is less tedious and filling a sample bottle is much faster with a consequent lower risk of airborne contamination while the bottle is open. The consumption of nitrogen gas is lower and the lower pressure minimizes disruption of particles. The filters have also a high capacity before clogging, of the order of several tens to hundreds of litres, depending on the particle load of the seawater. However, this filter type is not suitable for the analysis of particulate matter collected on the filter. For that, membrane filters are still necessary.

### General set-up of instrumentation

The analyzers presented here are small, cheap bench top instruments and can be used in conjunction with a laminar flow bench where samples and reagents are placed. A clean air van is then no longer necessary. The instruments (Fig. 1) are assemblies of commercially available components and were developed with the idea of making standardized manifolds with mutually exchangeable parts.

Our FIA instruments use in-line preconcentration by a 6 cm long, 3 mm id column containing immobilized 8-hydroxyquinoline on hydrophilic vinyl polymer (TSK-8HQ). It was prepared according to the method of Landing *et al.*<sup>21</sup> using Toyopearl HW-40C resin (TosoHaas, Germany). The column was installed in the sample loop of a Valco (VICI, Switzerland) six port Teflon rotary valve on an electrical actuator. A

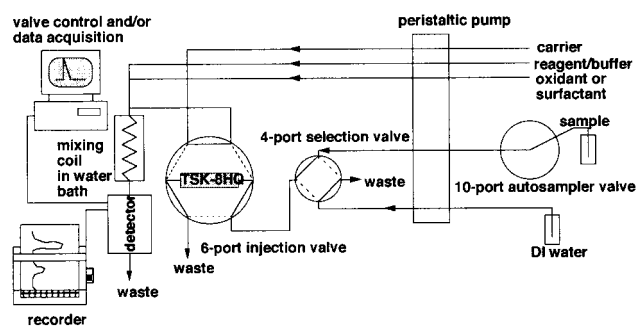


Fig. 1 Generalized scheme of the standardized FIA manifolds.

**Table 1** FIA reagents and applied flow rates

Application	Sample/MQ	Carrier	Reagent <sup>a</sup>	System buffer	Oxidant	Surfactant	Detector
Fe-FIA <sup>17</sup>		0.3 M HCl	0.3 mM luminol 0.3 mM TETA	0.6 M NH <sub>4</sub> OH	0.5 M H <sub>2</sub> O <sub>2</sub>	—	Hamamatsu H6240-01 photon counter
Flow/ml min <sup>-1</sup>	3.9 <sup>b</sup>	1.0	1.0	1.0	1.0		
Al-FIA <sup>22</sup>		0.05 M HCl	50 µM lumogallion	2 M NH <sub>4</sub> Ac (+ reagent)	—	2.5% Brij-35	Waters 470 fluorometer
Flow/ml min <sup>-1</sup>	2.5	1.2	0.32			0.32	
Mn-FIA <sup>23</sup>		0.08 M HCl	140 µM LMG	2 M NH <sub>4</sub> Ac	10 mM KIO <sub>4</sub>	—	CamSpec M220 spectrophotometer
Flow/ml min <sup>-1</sup>	3.9	0.32	0.32	0.32	0.32		
Mn-FIA <sup>24</sup>		0.05 M HCl	20 mM tiron 20 mM 2,2'-dipyridyl	0.25 M NaBO <sub>4</sub> (+ reagents)	0.2 M H <sub>2</sub> O <sub>2</sub>	—	CamSpec M220 spectrophotometer
Flow/ml min <sup>-1</sup>	2.5	0.32	0.32		0.32		

<sup>a</sup>Luminol (3-aminophthalhydrazide), TETA (triethylene tetramine), lumogallion (4-chloro-6-[(2,4-dihydroxyphenyl)azo]-1-hydroxybenzene-2-sulfonic acid), LMG (Leucomalachite Green), tiron (disodium-4,5-dihydroxy-1,3-benzenedisulfonate). The organic chemicals were used as received without further purification. The other reagents (*e.g.* hydrochloric acid, ammonia, acetic acid, hydrogen peroxide) were purchased from Merck, suprapure grade. <sup>b</sup>+0.1 M NH<sub>4</sub>Ac at 0.32 ml min<sup>-1</sup>.

peristaltic pump (Gilson Minipuls 3) is continuously delivering acidified sample, sample buffer, acid carrier, reagents and rinsing MQ. The pump runs at 8 rpm to reach nominal flow rates for the various tubing used for the various solutions (Table 1). High density polyethylene reagent bottles (Nalgene), polypropylene reagent straws (Bran & Luebbe, Netherlands), polycarbonate connectors (Cole-Parmer, USA) and PVC pump tubing were used, while all the other tubing was 0.8 mm id Teflon FEP. The systems are all cleaned by slowly pumping 0.5 M HCl for a minimum of 1 h, followed by rinsing with MQ water. In Table 1 an overview is given of the used reagents per FIA application.

During a loading time of 4 min buffered sample passes over the column. A four port selection valve switches to rinse the column with MQ water for 1 min to remove possibly interfering sea-salts. The injection valve then switches to the elute position and the acid carrier releases the analyte into the reagent stream towards the flow cell of the detector. One cycle of loading, rinsing and injection takes about 9 min. Auto-sampler valve (10-port), selection valve and injection valve are controlled *via* a home-made interface by software developed at the institute. The software was made in Visual BASIC running under Windows 95. Usually, with one batch of reagents, 5 standard additions and 25 samples can be measured, taking about 9 h. Finally the reagent stocks are replenished and the system is re-calibrated for a new run. Blank correction is done by subtracting an MQ rinse blank and a reagent blank that is caused by the addition to the sample of acid and buffer. The latter is determined by double spiking a sample with acid and buffer.

## Results and discussion

### Iron

The detection in this Fe-FIA application is based on the chemiluminescence produced by the iron catalyzed oxidation of luminol (3-aminophthalhydrazide, Fisher Acros) by hydrogen peroxide (Merck, suprapure). The ligand triethylene tetramine (TETA, Fisher Acros) was used as a sensitizer. For further details on the method and reagent preparation see elsewhere.<sup>17</sup> It should be noted that this FIA application features in-line buffering prior to introduction of the seawater sample into the preconcentration column. This was done to minimize the time between buffer addition and preconcentration as we found evidence that at the optimal preconcentration pH for Fe and 8-hydroxyquinoline, strong natural iron binding ligands could compete with the ligands of the preconcentration column, leading to a lower recovery and to faulty calibration data.

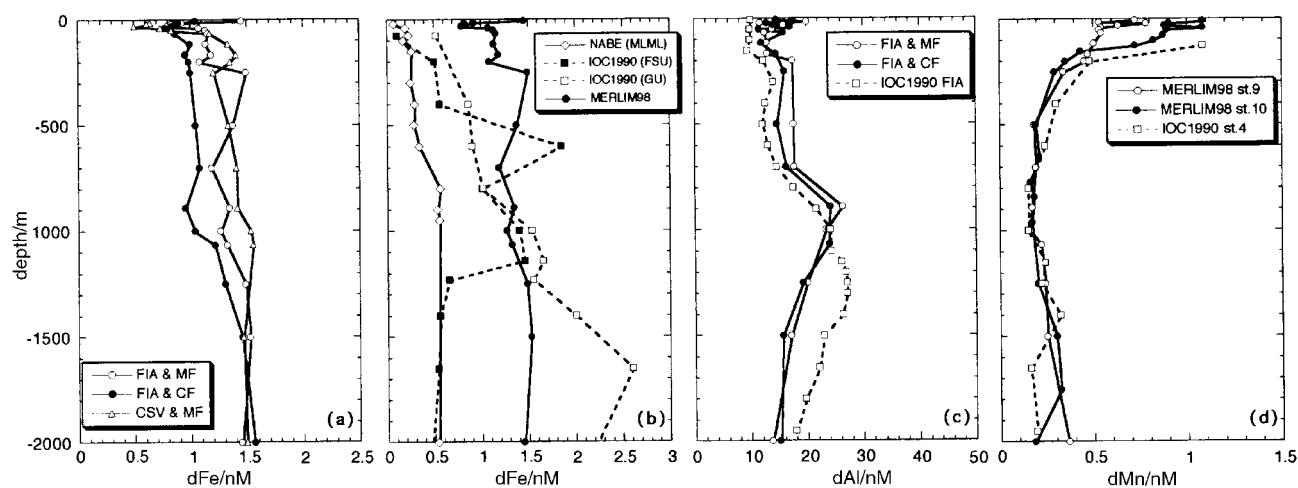
**Sampling and filtration.** During the R.V. *Pelagia* cruise MERLIM98 (Marine Ecosystem Regulation by limitation of carbon dioxide and trace metals) from March 2 until March 27, 1998, samples were taken in the Northeast Atlantic Ocean from the sea surface and at a number of stations along the 23°W meridian from 43°N until 37°N. See Nolting *et al.*<sup>25</sup> for a detailed map.

Surface sampling using the tow fish was compared with sampling by filling a bottle from a rubber boat ('zodiac'), which was moving parallel to the ship at the same speed of 5 knots. Samples were taken simultaneously at every 10 min for about 1 h. The zodiac sample was membrane filtered upon return on board using a polycarbonate Sartorius filtration device, supplied with Teflon O-rings. The results are essentially similar (zodiac:  $0.99 \pm 0.22$  nM,  $n=5$ ; fish:  $0.87 \pm 0.03$  nM,  $n=5$ ), but the smaller standard deviation on the fish data suggests less susceptibility for contamination. Apparently sample manipulations increase the chance of random contamination.

At two stations, station 9 (40°N, 23°W) and station 10 (37°N, 23°W), two types of filtration were compared: cartridge filtration (CF) and membrane filtration (MF). The vertical profile (18 depths between 0–2000 m) of station 9 is shown (Fig. 2a). Plotting all the vertical CF and MF data gives the relationship as shown in Fig. 3a, with MF data often being about 15% higher than CF. This may be due to rupture of fragile biogenic particles (*e.g.* phytoplankton cells, organic debris) by using a higher pressure with MF, or the simple pushing of small particles through the filter. Our results suggest that CF would be the better way of defining dissolved metal species.

**Analytical performance.** The regression lines of standard additions ( $n=5$ ) have excellent fits ( $r>0.99$ ) demonstrating uniform extraction efficiency at each added concentration. To examine the desired 100% efficiency, *i.e.* complete retention of Fe in the column, the same seawater sample containing 0.6 nM was run with different sample loading (using pump tubing with different flow rates, without changing the rpm of pump or loading time). In case of retention of less than 100%, at a higher flow rate the iron would remain in the column for less time and would therefore bind less efficiently, leading to a lower recovery. If the system response is plotted against the sample load this would lead to a curved line. However, the experiment resulted in a straight line (Fig. 4), suggesting that the retention was complete already from the highest sample loading. Or, less likely, the retention remained equally incomplete at every flow rate. Arguing against the latter are our earlier findings<sup>17</sup> concerning the 95% efficiency breakthrough capacity in seawater of a similar column at high flow rate. The TSK-8HQ





**Fig. 2** (a) Vertical profile of dissolved Fe showing results for membrane filtration (MF) and cartridge filtration (CF) as measured by Fe-FIA at MERLIM98 station 9 (40°N, 23°W), together with CSV results for the membrane filtered samples. (b) Dissolved Fe: MERLIM98 station 9 compared with other datasets: NABE (47°N, 20°W) by Moss Landing Marine Laboratories (MLML)<sup>26</sup> (three data points with higher concentrations at 200, 1100 and 1500 m were rejected and not published<sup>27</sup>), IOC1990 station 4 (34°N, 13°W) by Florida State University (FSU),<sup>28</sup> same by Gothenburg University (GU).<sup>28</sup> (c) Vertical profile of dissolved Al, results for MF and CF as measured by Al-FIA at MERLIM98 station 9, together with Al-FIA results from IOC1990 station 4.<sup>28,29</sup> (d) Vertical dissolved Mn compared: MERLIM98 stations 9 and 10, as well as averaged results from IOC1990 station 4.<sup>28</sup> FIA-method *cf.* Mallini and Shiller.<sup>24</sup>

column used here is capable of quantitatively binding at least 96 nmol of Fe. With the sample we used, an absolute amount of only 9.6 pmol is retained on the column, thus safely within the range where Fe is still retained quantitatively.

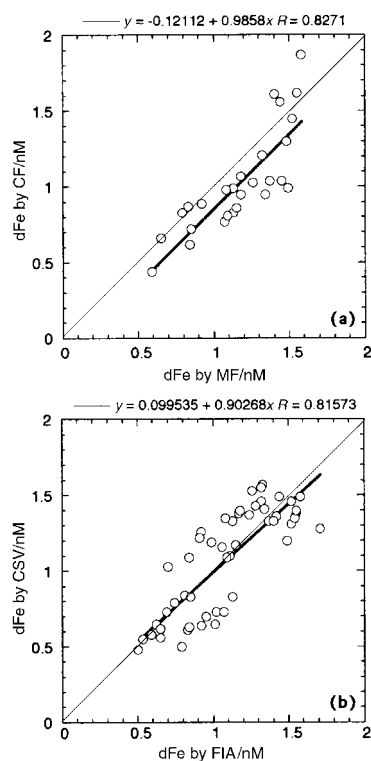
Sensitivity in different types of seawater was tested by comparing calibration lines made up in surface seawater sampled by tow fish from the Northeast Atlantic (batch of 20 l of seawater sampled March 1998 at approximately 43°N, 23°W) and the Antarctic (batch of 20 l of seawater sampled May 1999 at 50°S, 20°E) and measured in the same autosampler run. Standard additions of 0, 0.9, 1.8, 2.7 and

3.6 nM Fe were made. Calibration slopes were the same within 3.5% precision: 1 151 200 counts nM<sup>-1</sup> ( $r=0.996$ ) for the Atlantic water and 1 085 400 counts nM<sup>-1</sup> ( $r=0.993$ ) for the Antarctic water. However, long term sensitivity appears to be less constant (Table 2), around 20% variability seems to be common. The reason for this could be a combination of small differences in reagent composition, reagent aging, or pump tubing quality, influencing reagent mixing characteristics. It can be assumed that these changes equally influence standard additions and samples.

Blanks and detection limit are given in Table 3 and are sufficiently low to measure subnanomolar oceanic concentrations.

**Accuracy checks.** Reference seawater samples from the National Research Council of Canada (NRCC), NASS-4, NASS-5 and CASS-3, were measured regularly (Table 4) with satisfying accuracy. These certified samples cover a wide range of Fe concentrations (1.9, 3.7, and 23 nM, respectively), however all are above the Fe concentrations typically found in open ocean waters (<1 nM). Therefore, during the above mentioned MERLIM98 cruise an intercalibration exercise was done on board by measuring the same low concentration samples with FIA and cathodic stripping voltametry (CSV).

To describe the CSV method briefly, a synthetic ligand (1-nitroso-2-naphthol, Fluka, Germany) is added in large amount to the seawater sample free of organic complexing matter, to bind iron, after which voltammetric analysis is carried out.<sup>30</sup> Previous methods recommend acidification and UV-digestion of the sample in order to destroy the dissolved complexing matter.<sup>31–34</sup> However, these two steps firstly involve sample manipulations, which might introduce contamination and secondly, the pH has to be buffered to 6.7–7.8<sup>35</sup> prior to the measurement by CSV. This might also introduce contamination by buffer addition and sample manipulations. Buffering could also cause iron colloids to precipitate,<sup>36</sup> possibly decreasing the apparent iron concentration. For these reasons, iron was UV-digested at the seawater pH. UV-digestion of the sample for at least 90 min (without acidification) has been shown to efficiently destroy the iron-binding capacity of the dissolved organic ligands.<sup>30,37</sup> The UV-digestion (using a 600 W high-pressure mercury-vapor lamp) was done on-line (flow rate of about 1 ml min<sup>-1</sup>), with a conventional digestion time of 2 h. Voltammetric measurement was carried out at



**Fig. 3** Iron. (a) Correlation between MF and CF. Data taken from MERLIM98 stations 9 and 10. (b) Correlation between FIA and CSV for all the vertical Fe data (MF) in the research area of the MERLIM98 cruise: stations 6 (37°N, 23°W), 8 (43°N, 23°W), 9 (40°N, 23°W) and 10 (37°N, 23°W).

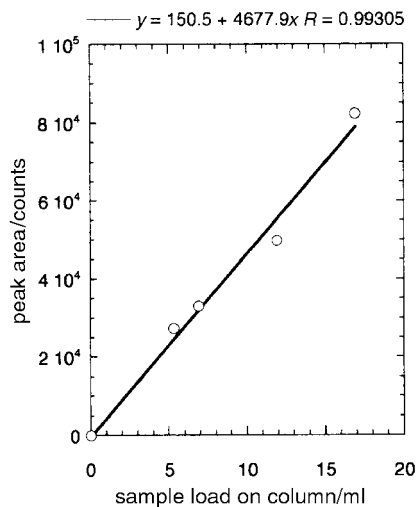


Fig. 4 Iron. System response *versus* sample loading on column.

Table 2 Typical FIA sensitivities (slope of calibration lines)

Cruise		Fe slope/ counts nM <sup>-1</sup>	Mn slope/ mm nM <sup>-1</sup>	Al slope/ mm nM <sup>-1</sup>
MERLIM98	Av	17 295 600	55.11	8.3
	s	3 977 930	9.61	1.53
	RSD (%)	23	17	18
	n	15	10	8
Ant XVI/3 (1999)	Av	10 290 794		9.07
	s	1 857 049		1.8
	RSD (%)	18		20
	n	31		9
IOC 1996	Av	10 166 406		
	s	1 973 813		
	RSD (%)	19		
	n	16		

pH 7.8 using HEPES buffer (Merck, final concentration 0.01 M), with 20 μM of 1-nitroso-2-naphthol (C<sub>10</sub>H<sub>6</sub>OHNO). The oxidant potassium bromate (KBrO<sub>3</sub>, 40 mM final concentration) was used to increase the sensitivity of the measurement.<sup>30</sup> The voltammetric procedure was carried out using sample-dc (40 mV s<sup>-1</sup>, step interval time 0.1 s), with a deposition potential of -0.1 V and a deposition time of 90–180 s.

As can be seen from Fig. 2a and 3b the results from these fundamentally different methods compared quite well, notwithstanding some scatter. This could be caused by differences in sample pretreatment (UV digestion *versus* acidification) and measurement principle. The fact that there are no real outliers, suggests that contamination control was sufficient.

There is a lack of published dissolved Fe data in the region for comparison with our results. The 1990 IOC intercalibration exercise at 34 °N, 13 °W was 8 years earlier, since then methods for sampling and filtration have greatly improved. This is most crucial for elements which are known to be most prone to

contamination, *e.g.* Fe, Zn, Pb as opposed to *e.g.* Mn (see below) or Ni. Indeed for dissolved Fe only two IOC groups reported their final values,<sup>28</sup> and these two data sets still differ by a factor 2 to 3 (Fig. 2b). It is hard to say who offers the most accurate data. An average of both sets gives more or less similar deep water (>500 m) values to those we found, but obviously with a very large error. This still leaves us with higher values for the upper water column (<500 m), which are ascribed to transient input from Sahara dust.<sup>38</sup> Shortly before arriving in our research area a Saharan dust storm had blown a large amount of aerosols into the ocean, consequently enriching the upper waters with trace elements. Evidence for this event was found by Seawifs remote sensing (Seawifs homepage at NASA: [http://seawifs.gsfc.nasa.gov/SEAWIFS/IMAGES/SEAWIFS\\_GALLERY.html](http://seawifs.gsfc.nasa.gov/SEAWIFS/IMAGES/SEAWIFS_GALLERY.html)).

During the May 1989 North Atlantic bloom experiment (NABE) a station at 47°N, 20°W<sup>26</sup> exhibited concentrations half those we report here. Also, this would be consistent with the stronger influence of Sahara dust input at our more southerly stations. This and a more or less permanent frontal system near about 42°N<sup>39</sup> may explain the higher Fe of our stations *versus* the 47°N site.

Aluminium

For the MERLIM98 cruise Al was measured by Al-FIA using fluorimetric detection of the Al-lumogallion complex (lumogallion: 4-chloro-6-[(2,4-dihydroxyphenyl)azo]-1-hydroxybenzene-2-sulfonic acid, ICN Biomedicals), according to the method of Resing and Measures.<sup>22</sup> The surfactant Brij-35 (Fisher Acros) was used as a sensitizer. Samples were buffered by manual addition of clean ammonium acetate buffer to obtain a final pH of 5.5. Peak height was measured from a Kipp BD111 recorder.

**Sampling and filtration.** As for Fe, CF was compared with MF (Fig. 2c), here only for station 9. Like Fe, MF was generally giving about 5% higher concentrations than CF for reasons already mentioned.

**Analytical performance.** Typical variation in calibration slopes of around 20% also occurred here, while blanks and detection limit were sufficient to measure low oceanic concentrations (1–10 nM) (Tables 2 and 3).

**Accuracy checks.** As there is no reference seawater available that is certified for dissolved Al content, one of the ways to get information on accuracy is to compare with existing profiles, as for instance from the already mentioned nearby IOC 1990 station 4.<sup>29</sup> Dissolved Al was at that time measured with a very similar FIA method. A common hydrographic feature in these waters is the presence of the so-called Mediterranean outflow water, a wedge of high salinity, high Al water flowing out of the adjacent Strait of Gibraltar. Its higher salinity (not shown) and higher Al content are determined by the high Mediterranean Sea end member.<sup>40</sup> At the IOC station its core was located between 1100 and 1400 m, while at the MERLIM98 stations it was between 800 and 1100 m. Note the similarity in the

Table 3 Typical blanks (nM) and detection limits for FIA methods (DL, defined as three times the standard deviation (s) of the blank)

Cruise		Fe blank	Fe DL	Mn blank	Mn DL	Al blank	Al DL
MERLIM98 (1998)	Mean ± s	0.09 ± 0.06	0.18	0.05 ± 0.03	0.09	0.31 ± 0.23	0.69
	n	3		7		4	
Ant XVI/3 (1999)	Mean ± s	0.04 ± 0.01	0.03	—	—	0.46 ± 0.18	0.54
	n	9		—		7	
IOC96 (1996)	Mean ± s	0.08 ± 0.05	0.15	—	—	—	—
	n	7		—		—	

concentrations and the trends that the profiles follow (Fig. 2c). Dust input in the upper part of the water column (see above) may have caused the higher values seen there. The differences in the deeper water may be the result of different hydrography at the two sites.

### Manganese

Two Mn-FIA methods have been used by us, starting with the spectrophotometric method of Resing and Mottl.<sup>23</sup> detection at 620 nm of the product of the manganese catalyzed oxidation of Leucomalachite Green by potassium periodate. Peak height was measured from a Kipp BD111 recorder. Confirming the findings of these investigators, typically slightly parabolic calibration curves were obtained (averaged curve fits/ $\text{mm nM}^{-1}$ :  $(18.9 \pm 4.5) + (47.8 \pm 10.9)X + (9.8 \pm 5.0)X^2$ ,  $n = 12$ ). However, later work was done with the spectrophotometric method of Mallini and Shiller.<sup>24</sup> This method was chosen because of a less complex FIA manifold, better reagent and baseline stability and linear calibration. Detection is based on the manganese catalyzed oxidation of tiron (disodium-4,5-dihydroxy-1,3-benzenedisulfonate, Fisher Acros) by hydrogen peroxide in the presence of 2,2'-dipyridyl (Fisher Acros), forming a colored product and being measured at 440 nm. For both Mn-FIA applications, an optimal preconcentration pH of  $8.0 \pm 0.2$  was reached by manually buffering aliquots of 100 ml acidified seawater with clean saturated Tris buffer.

**Sampling and filtration.** Coastal water column samples were collected on the R.V. *Hyas* and R.V. *Johan Ruud* during Spring 1996 at a station (69.3 °N, 19 °E) in the oxic Balsfjord near the city of Tromsø, Norway. Once or twice a week a surface sample or a vertical profile (190 m depth) was measured at this location between early April and early June so as to study the seasonal evolution of trace metal concentrations. After sampling with GoFlo's on a Kevlar wire, unfiltered subsamples were transferred on deck into clean 5 l PE bottles, using a closed system with Teflon tubing going through the sample bottle's

**Table 4** FIA results for reference seawaters NASS-4, NASS-5 and CASS-3

Date/d.m.y	Fe/nM	n	Date/d.m.y	Mn/nM	n
<i>NASS-4—</i>					
3.2.95	$2.02 \pm 0.34$	5	14.4.97	$7.18 \pm 0.09$	2
15.2.95	$1.55 \pm 0.12$	2	15.4.97	$6.61 \pm 0.02$	2
3.4.95	1.91	1	16.4.97	$6.98 \pm 0.06$	3
11.4.95	1.97	1	16.12.98	$7.38 \pm 0.01^a$	2
18.9.96	$1.79 \pm 0.08$	5			
3.2.98	$1.79 \pm 0.05$	2			
4.2.98	$2.28 \pm 0.20$	2			
Mean of means	$1.90 \pm 0.21$	7		$7.04 \pm 0.28$	4
Certified value	$1.88 \pm 0.29$			$6.92 \pm 0.43$	
<i>NASS-5—</i>					
30.9.98	$3.95 \pm 0.04$	2	16.12.98	$18.28 \pm 0.78^a$	2
29.3.99	$2.48 \pm 0.02$	2			
20.7.99	$3.96 \pm 0.76$	6			
2.8.99	$3.17 \pm 0.23$	4			
24.8.99	$3.69 \pm 0.57$	6			
31.8.99	$3.05 \pm 0.08$	2			
2.9.99	$2.87 \pm 0.04$	2			
7.9.99	$3.70 \pm 0.50$	4			
Mean of means	$3.35 \pm 0.51$	8		$18.28 \pm 0.78$	2
Certified value	$3.71 \pm 0.63$			$16.73 \pm 1.04$	
<i>CASS-3—</i>					
6.12.98	$24.9 \pm 0.7$	2	14.4.97	$50.48 \pm 0.64$	2
			15.4.97	$50.35 \pm 1.40$	2
			16.12.98	$44.91 \pm 4.27^a$	2
Mean of means	$24.9 \pm 0.7$	2		$48.58 \pm 2.60$	3
Certified value	$22.6 \pm 3.0$			$45.69 \pm 6.55$	

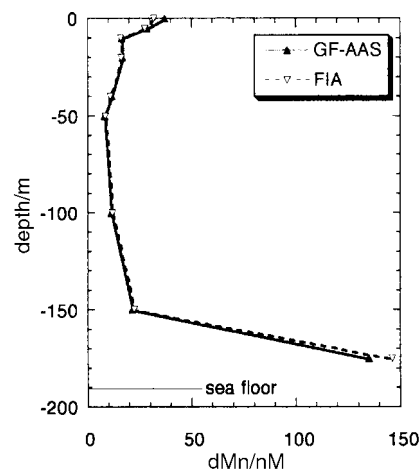
<sup>a</sup>Mallini and Shiller's method.<sup>24</sup>

screw cap. All parts were rinsed with ample amounts of seawater. The samples were brought back to the clean air van, which was this time land-based due to the small size of the research vessels. Immediately the samples were 0.1  $\mu\text{m}$  membrane filtered in a Sartorius polycarbonate filtration device refitted with Teflon O-rings. Samples were acidified ( $\text{pH} < 2$ ) with clean nitric acid and stored in a refrigerator. The Balsfjord samples contained relatively high concentrations of Mn and were therefore initially measured by direct injection GFAAS measurement. A Perkin-Elmer 5100 graphite furnace AAS with Zeeman background correction was used, without matrix modifier. The method of standard additions was applied using standards made up in 0.05 M HCl. Injected sample volume was 25  $\mu\text{l}$  and measurement was done in triplicate. Detection limit was 2 nM Mn. One year later the samples were re-analyzed using the FIA-method described by Resing and Mottl.<sup>23</sup>

For the MERLIM98 cruise only membrane filtered manganese was measured with the FIA-method described by Mallini and Shiller.<sup>24</sup> No comparison between MF and CF was done for this metal.

**Analytical performance.** As in the case of Fe-FIA and Al-FIA, calibration line slopes (Table 2) showed a long term variability of around 20%. Blanks and detection limits (Table 3) were very low and reproducible. Judging from the results for reference seawater (Table 4) good accuracy was obtained for both FIA applications.

Results from a typical station (ARC15) in the Balsfjord is shown in Fig. 5, with both the GFAAS and FIA results. The profile features surface enrichment due to fresh water input from land, following snow melt. Near the bottom a dramatic increase indicates a flux of reduced manganese from the anoxic sediments. The regression using the data points from all stations, shows a good correlation:  $-2.02 + 1.1136X$ ,  $r = 0.9902$ ,  $n = 59$ . There is a slight off-set of about 2 nM, probably a result of imperfect calibration blank correction of the much less sensitive GFAAS (detection limit  $\sim 2$  nM). The only two samples with concentrations higher than 40 nM gave GFAAS data that were lower by about 8%. This may have been caused the fact that these samples gave AA signals higher than the highest standard and were therefore automatically diluted by the autosampler, introducing an off-set due to a possible combination of a systematic dilution error and lesser salt matrix effects. Bottle artifacts resulting from the long storage time can be ruled out, as this would show more dramatically, and with much more scatter, at the lower concentrations, which is not the case. The 8% difference should also be seen relative to



**Fig. 5** Manganese. Vertical profile of dissolved Mn at station ARC15 in the Norwegian Balsfjord on June 4, 1996 as measured by Mn-FIA and GFAAS. FIA-method cf. Resing and Mottl.<sup>23</sup>

usual precisions of 5% for GFAAS determinations in seawater, and of 2% or better for FIA.

The consistency of the MERLIM98 manganese results was demonstrated by comparing them with the average values obtained during the above mentioned IOC 1990 intercalibration cruise (Fig. 2d).<sup>28</sup> Going from north to south, thus approaching the Saharan dust input source, the surface manganese increases.

## Conclusions

The proposed FIA methods for Fe, Mn and Al are found to be very suitable for high sensitivity shipboard measurement of the lowest existing concentrations in the oceans. For surface sampling we recommend in-line cartridge filtration of seawater pumped on board by a tow fish while the ship is underway. The same cartridge filtration can also be applied to water column samples that have been taken by conventional sampling using GoFlo water samplers on a Kevlar wire. Cartridge filters can not be used if analysis of suspended particulate matter is required.

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